

**Final**

**Summary of Research**

**On**

**“Novel High Efficient Organic Photovoltaic Materials”**

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## Summary of Research

The objectives and goals of this project were to investigate and develop high efficient, lightweight, and cost effective materials for potential photovoltaic applications, such as solar energy conversion or photo detector devices. Specifically, as described in the original project proposal, the target material to be developed was a block copolymer system containing an electron donating (or p-type) conjugated polymer block coupled to an electron withdrawing (or n-type) conjugated polymer block through a non-conjugated bridge unit. Due to several special requirements of the targeted block copolymer systems, such as electron donating and withdrawing substituents, conjugated block structures, processing requirement, stability requirement, size controllability, phase separation and self ordering requirement, etc., many traditional or commonly used block copolymer synthetic schemes are not suitable for this system. Therefore, the investigation and development of applicable and effective synthetic protocols became the most critical and challenging part of this project.

During the entire project period, and despite the lack of a proposed synthetic polymer postdoctoral research associate due to severe shortage of qualified personnel in the field, several important accomplishments were achieved in this project and are briefly listed and elaborated below. A more detailed research and experimental data is listed in the Appendix attached.

1. A number of terminal functionalized and alkylsulfone (acceptor) derivatized poly(1,4)phenylenevinylenes (SF-PPV-I) blocks have been successfully synthesized and characterized. Most importantly, the SF-PPV-I block size control below the average organic exciton diffusion length of 30 nanometers has also been demonstrated.
2. A number of terminal functionalized and alkyloxy (donor) derivatized poly(1,4)phenylenevinylenes (RO-PPV) blocks have been successfully synthesized and characterized. Most importantly, the RO-PPV block size control below 30 nanometers has also been demonstrated.
3. Spectroscopic and electrochemical studies demonstrated that the molecular orbital (*i.e.*, HOMO and LUMO) energy level differences of SF-PPV-I and RO-PPV blocks indeed form a good exciton dissociation (or electron-hole separation) potential interface.
4. The SF-PPV-I and RO-PPV blocks have been successfully coupled covalently via two different aliphatic bridges. To our knowledge, this is the first demonstration of a block copolymer system where an electron donating conjugated polymer block is coupled to an electron withdrawing polymer block via a non conjugated bridge unit.
5. Block copolymer nano phase separation pattern was also observed in preliminary electron microscopic studies.
6. The progress of the project has attracted additional new grants so that the materials system can be further developed and prototype devices can be further evaluated.
7. The project also generated broad positive impact to education and to the society via publications and presentations in the scientific community.

## 1. Alkylsulfone derivatized polyphenylenevinylenes (SF-PPV-I) acceptor blocks

For the acceptor (n-type) block, the target structures must meet the following criteria as proposed: 1) the block backbone must be a  $\pi$ -electron conjugated system, so that the exciton HOMO-LUMO optical absorption can be at visible or infrared wavelengths (main range of solar radiation), charge carriers can couple or transfer more effectively via conjugated orbital, and  $\pi$ -stacking may yield favorable molecular self-assembly. 2) the electron withdrawing substituents (acceptor) must be attached to the block backbone, and 3) the terminal of the block must be functionalized in order to be able to covalently couple with other blocks, and 4) the block size must be controllable, so that the nano phase domain size can be controlled within the effective or average exciton diffusion range (typically less than 30 nm).

While there were a number of acceptor conjugated systems mainly including cyano derivatized polyphenylenevinylenes (CN-PPV) or C60 were reported before, yet few reports have systematically investigated or demonstrated the block size control, and the terminals of those reported systems were not functionalized or not able to be functionalized. Therefore, they could not be coupled into the block copolymer system we proposed.

In our synthetic approach, we employed Wittig type reaction to synthesize alkyloxy (donor) substituted diphosphate monomer units first and coupled it to a benzene dialdehyde co-monomer unit to build the donor block (shown in Appendix). In this way, both the block size and the terminal functional groups can be controlled simply by changing the molar ratio of the two co-monomers. For instance, the terminal functional groups of the blocks would be the same as monomers in access, and the bigger the difference of the monomer ratio, the shorter the block size. Details of the experimental results and data are listed in Appendix.

## 2. Alkyloxy derivatized polyphenylenevinylenes (RO-PPV) donor blocks

For the donor (p-type) block, the target structures must meet the following criteria as proposed: 1) the block backbone must be a  $\pi$ -electron conjugated system, so that the exciton HOMO-LUMO optical absorption can be at visible or infrared wavelengths (main range of solar radiation), charge carriers can couple or transfer more effectively via conjugated orbital overlaps, and  $\pi$ -stacking may yield favorable molecular self-assembly. 2) the electron donating substituents (donor) must be attached to the block backbone, and 3) the terminal of the block must be functionalized in order to be able to covalently couple with other blocks, and 4) the block size must be controllable so that the nano phase domain size can be controlled within effective or average exciton diffusion range.

While there were a number of donor conjugated polymers including some alkyloxy derivatized polyphenylenevinylenes reported before, yet few reports have systematically investigated or demonstrated the block size control, and the terminals of

those reported systems were not functionalized nor able to be functionalized, therefore they could not be coupled into the block copolymer system as proposed.

In our synthetic approach, we again employed Wittig type reaction to synthesize the alkyloxy (donor) substituted diphosphate monomer units first and then coupled it to a benzene dialdehyde co-monomer unit to build the donor block (shown in Appendix). In this way, both the block size as well as terminal functional groups can be controlled by changing the mole ratio of the two co-monomers. For instance, the terminal functional groups of the blocks would be the ones on the monomers in excess, and the bigger the difference of the monomer ratio, the shorter the block size. Details of the experimental results and data are listed in Appendix.

### **3. Molecular Orbital Level Characterizations of SF-PPV-I and RO-PPV blocks**

Electrochemical (*e.g.*, cyclic voltammetry) and spectroscopic (UV-VIS absorption, luminescence spectrometry) analysis results revealed that SF-PPV-I has a LUMO level of  $-3.6$  eV and a HOMO level of  $-6.0$  eV, while RO-PPV has a LUMO level of  $-2.7$  eV and a HOMO level of  $-5.2$  eV. The potential difference between the RO-PPV and SF-PPV-I at LUMO level is  $0.9$  eV, and at HOMO level is  $0.8$  eV, well exceeds the expected minimum organic exciton dissociation potential of  $0.5$  eV. Thus SF-PPV-I and RO-PPV indeed formed a desired organic P/N system. Details of results see Appendix.

### **4. SF-PPV-I and RO-PPV blocks was successfully coupled covalently via two different aliphatic bridges.**

To our knowledge, this is the first demonstration of a block copolymer system where an electron donating conjugated block is coupled to an electron withdrawing conjugated block via a non-conjugated bridge unit. A non-conjugated and flexible bridge unit is critical for two reasons: 1) it retards the electrons in acceptor block from recombining with holes in donor block via conjugated backbones, and 2) it helps to reduce the conjugation distortion in either donor or acceptor block by providing a flexible junction point. The synthetic strategy we used here was to use excess bridge unit (B) couple with either a donor (D) or acceptor (A) block first to form  $-BDB-$  or  $-BAB-$ , then couple with equal amounts of A (in case of  $-BDB-$ ) or D (in case of  $-BAB-$ ) to form the final  $-BDDB-$  block copolymer. Since the UV-VIS absorption spectra of final  $-BDDB-$  block copolymers were almost the simple overlap of UV-VIS of donor and acceptor blocks, charge separation (electron transfer) via donor/acceptor interface at ground states (non-excited states) were not obvious. On the other hand, photo induced luminescence (PL) of  $-BDDB-$  block copolymer were quenched nearly 99% in comparison to pristine donor or acceptor blocks in solid thin film states. This demonstrated very effective or efficient photo induced exciton charge dissociation (or electron-hole separation) due to the presence of donor-acceptor interfaces. The exciton charge dissociation is a very critical step in organic photovoltaic process. Details of the results and data are in Appendix.

### **5. Block copolymer nano phase separation**

For photovoltaic device purposes, a donor-acceptor bi-continuous phase separated morphology is very critical to ensure a smooth and continuous transportation path ways for electrons reaching the negative electrode and holes reaching the positive electrode. A key rational for this project is that block copolymer is well known for its tendency to form a bi-continues phase separated morphology. However, block copolymer phase separation is dependent on several factors such as block size, chemical or structural difference between blocks, processing conditions, etc. For one of our synthesized – DBAB- final block copolymer sample, a unique nano phase separated pattern was seen under electron microscope. Details of the data are in Appendix.

## **6. New funding for the project**

Due to the significance and the progress of this project, AFOSR has awarded new grants to continue support on these research efforts. These new grants will not only enable the already developed materials system to be further optimized and improved, but they will also enable better materials structures and prototype photovoltaic devices from these materials to be developed and evaluated.

## **7. Broader positive impact or other benefits from the project.**

This research grant also trained our students and promoted the development of the field in a much broader scale via classroom teaching, research seminars, conference presentations, publications and research exchanges in scientific communities. For instance, in addition to reports and presentations to funding agency, research generating new knowledge was also disseminated at university classrooms, seminars, other academic institutions, or presented/published at international scientific communities, such as the American Chemical Society, International Society for Optical Engineering, International Conference on Synthetic Metals, etc. At least seven papers (four peer reviewed) have already been published or in press at journals or major conference proceedings (see references listed below). More papers are in preparation for publications or presentations. At least four master degree graduate students and over four undergraduate students participated in this project and made presentations at national or international conferences. The positive impact of this project for attracting potential next generation scientists into this field is hard to measure. Finally, as a result of this project, NSU also became an affiliated member and hosted a national conference for the Consortium of Advancing Renewable Energy Technology (CARET) in September 2000.

In summary, significant progress has been accomplished for this project in a relatively short period of time. As the project proposed and recent progress demonstrated, this project is critically important for the future of human being as it directly addresses two critical issues of our era: energy and environment. Therefore, more research efforts should be pursued, and more support is needed in this area.

## **8. Project Related Publications/Presentations**

- [1] Sun, S.; Fan, Z.; Wang, Y.; Taft, C., “A novel -DBAB- type block copolymer”, plan to publish at *J. Am. Chem. Soc.*, in preparation.

- [2] Wang, Y.; Fan, Z.; Taft, C. and Sun, S., “A New Acceptor (n-Type) Polyphenylenevinylene Building Block: SF-PPV-I”, *Chem. Mater.*, submitted.
- [3] Sun, S.; Fan, Z.; Wang, Y.; Taft, C.; Haliburton, J.; Maaref, S.; “Synthesis and Characterization of a Novel –DBAB- Block Copolymer System for Light Harvesting Applications”, *SPIE*, **2002**, vol. 4801, in press, and presentation at SPIE 2002 annual convention, Seattle, Washington, July, 2002.
- [4] Sun, S.; Fan, Z.; Wang, Y.; Haliburton, J.; Taft, C.; Seo, K.; Bonner, C., “Conjugated Block Copolymers for Opto-Electronic Functions”, *Syn. Met.*, **2002**, in press, and presentation at the International Conference on Synthetic Metals ‘ICSM2002’ at Shanghai, China, June, 2002.
- [5] Sun, *et al.*, “Organic and Polymeric Electro-active Materials”, an invited seminar presentation at a joint chemistry/physics departmental seminar at Hampton University, Virginia, USA, April 4, **2002**.
- [6] Fan, Z.; Wang, Y.; Taft, C.; Haliburton, J.; Maaref, S. and Sun, S., “Synthesis and Characterization of a novel block copolymer containing donor and acceptor blocks”, *Poly. Mat. Sci. Eng.*, **2002**, 86, 47.
- [7] Wang, Y. and Sun, S., “Synthesis and Characterization of SF-PPV I”, *Poly. Mat. Sci. Eng.*, **2002**, 86, 67.
- [8] Ma, J.; Song, H.; Frisch, H. L; Maaref, S.; Sun, S., “Electrically Conductive Semi-IPNs Based on Polyaniline and Crosslinked Polyvinylacetate”, *J. Appl. Poly. Sci.*, **2002**, 85(11), 2287-2293.
- [9] Sun, S.; Fan, Z.; Wang, Y.; Taft, C.; Haliburton, J.; Maaref, S.; “Design and Synthesis of Novel Block Copolymers for Efficient Opto-Electronic Applications”, *SPIE*, vol. 4465, pp 121-128, **2001**, and presentation at SPIE 2001 annual convention, San Diego, California, July 2001.